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TITLE: Optical Nonlinearity of Sputtered Co3O4-SiO2-TiO2 Thin Films

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Mat. Res. Soc. Symp. Proc. Vol. 703 © 2002 Materials Research Society V13.20

Optical Nonlinearity of Sputtered Co_3O_4-SiO_2-TiO_2 Thin Films

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ABSTRACT

Optical non-linearity of cobalt oxide with SiO_2-TiO_2 additives was investigated, and the change mechanism of the refractive index (n) and extinction coefficient (k), based on the relation between band structure and optical non-linearity of the thin films, was discussed. Refractive index and extinction coefficient of Co_3O_4 thin films in the ground state were 3.17 and 0.42, respectively. Both n and k decreased by irradiation from a pulse laser with 650 nm of wavelength (1.91eV). These values in the excited state were 2.91 and 0.41, respectively. n_2 estimated from the change of n and k was -2.8×10^{-11} m^2/W. The film had a band gap corresponding to 2.06eV, indicating that it was widened by the band filling effect during the laser irradiation at 1.91eV, and this led to the decrease in absorption coefficient and refractive index.

INTRODUCTION

Spectral analyses [1-3], band structural analyses [4-6] and optical nonlinearity [7], of cobalt oxide thin films have been extensively reported. Recently, we have discovered that cobalt oxide thin films containing glass additives have remarkable optical nonlinearity, that is, their refractive index drastically changes with laser irradiation (λ=650nm, E=1.91eV) [8-11]. Therefore these films are suitable as super resolution films to reduce the spot size of the laser irradiated on optical recording media such as DVDs (digital versatile disks). Furthermore, we have reported the nano structure of some of these thin films and found they had nano-scale Co_3O_4 precipitated particles with an amorphous grain boundary phase of 1.0nm width [12].

Ando et al. [7] investigated the third order nonlinear optical susceptibility $\chi^{(3)}$ of thin films of transition metal oxides including Co_3O_4 with a phase-conjugation-type degenerate four-wave mixing (DFWM) method. They reported that thin films of transition metal oxides had large $\chi^{(3)}$ when 7ns and 35ps pulse lasers with a wavelength of 532nm were irradiated on them. Co_3O_4 showed significantly more nonlinearity than the other transition metal oxide films because of its high figure of merit, $\chi^{(3)}/\alpha$.

In the present study, refractive index and extinction coefficient of ground and excited states were measured by an ellipsometric method to investigate the mechanism of non-linearity of Co_3O_4-SiO_2-TiO_2 thin films.

EXPERIMENTAL PROCEDURE

Thin films of Co_3O_4 with SiO_2 and TiO_2 additives were obtained by RF magnetron sputtering at room temperature on borosilicate glass substrates. Composition of the film was

$84Co_3O_4$-$8SiO_2$-$8TiO_2$ in molar percentage. An SPF-430H sputtering device (Anelva Co. Ltd.) was used to form the thin films. Sputtering gas was argon including 10 vol% O_2 and sputtering power was 600W on a 101.6 mm ϕ target. Thickness of each film was about 70nm. Back pressure was under 1.0×10^{-4} Pa, and the pressure during sputtering was 6.7×10^{-1} Pa.

Nano structure was evaluated by transmission electron microscopy (TEM; Hitachi H-9000NAR). The acceleration voltage was 300 kV. The TEM specimens were prepared by an ion milling device (Gatan Model 600 N).

We introduced a new device to measure refractive index (n) and extinction coefficient (k) in the ground and exited states. Ltd. The device had an ellipsometric optical arrangement. The ellipsometer (type DHA-NP) was designed and manufactured by Mizojiri Optical Co. The optical source was a semiconductor laser with a wavelength of 650nm. A laser driver drove the laser source and a pulse generator changed the laser power. Pulse width was 100ns. The laser beam was irradiated onto the specimen through a polarizer and focusing lens. Then the beam reflected onto the surface of the thin film specimen, and then passed through an analyzer and filter before reaching the detector. The signal was sent to a digital oscilloscope with a sampling frequency of 0.5GHz. One measurement was repeated 128 times and the average was sent to a PC, and Δ, ϑ, and n, k were calculated. Laser intensity (I) for measuring n and k in the ground state was under $0.13 GW/m^2$ and between $1.0 GW/m^2$ and $9.0 GW/m^2$ for measuring them in the excited state.

Optical transmittance spectra of the films were measured by an optical spectrum analyzer (Hitachi, U-3500). Transmittance of the substrate was subtracted as the base line. Optical absorption spectra were calculated from the transmittance spectra.

RESULTS

A high-resolution TEM image from a plane view of the $84Co_3O_4$-$8SiO_2$-$8TiO_2$ film indicated that the film consisted of nano-scale particles with a grain boundary phase. Average grain size (d) of the film was 10.7nm, and the standard deviation (σ) of the grain size of the sample was 2.14nm. The selected area diffraction images of the film corresponded to the diffraction patterns of Co_3O_4.

Figure 1 shows the change of n and k induced by laser pulse irradiation (wavelength, 650nm). The intensity of the pulse laser started to increase at t=0, and it rose to $9.0 GW/m^2$. With increasing pulse laser intensity, n decreased from 3.17 to 2.91. On the other hand, k was almost constant for the duration of the pulse laser irradiation.

Laser power dependence of n and k of the thin film are shown in Figure 2. Refractive indexes decreased as a function of laser intensity. The extinction coefficient slightly decreased with increasing laser power.

We reported that n and k, estimated using optical disk style samples, decreased from 2.53 to 2.23 and from 0.66 to 0.40, respectively with increasing laser intensity [11]. Although absolute values of n and k differed between the two methods, directions and extents of the changes of n and k were similar, that is, n and k decreased with increasing laser intensity.

Next, we dealt with this phenomenon in terms of optical nonlinearity. The nonlinear refractive index is described as follows:

$$n = n_0 + n_2 I \qquad (1)$$

where n_2 is nonlinear refractive index, I is laser power and n_0 is the linear refractive index when laser power is weak. In the $84Co_3O_4$-$8SiO_2$-$8TiO_2$ film, $n_0=3.17$ and $n=2.91$, so $n_2 I=-0.26$. Further, $I=9.0 GW/m^2$, hence n_2 was calculated as -2.8×10^{-11} m^2/W.

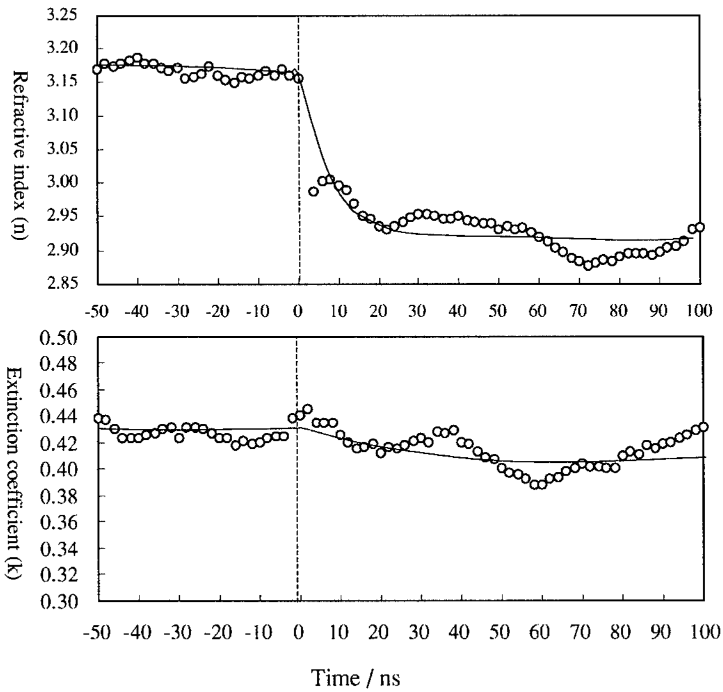

Figure 1 Change of refractive index and extinction coefficient of $84Co_3O_4$-$8SiO_2$-$8TiO_2$ thin film by laser irradiation.

To investigate the change mechanism of the refractive index and extinction coefficient of Co_3O_4 films, we analyzed optical absorption spectra. Figure 3 plots $(\alpha h\nu)^2$ versus $h\nu$ of these films. Eg values were calculated in accordance with the method shown in Ref. 2. Each film had a straight line portion, and extrapolation of the line to zero absorption coefficient was close to Eg=2.0 eV. The Eg values showed good agreement with the previous findings [2].

DISCUSSION

As we mentioned above, both n and k decreased as a function of laser pulse intensity. One of the mechanisms that can describe this phenomenon is the band filling effect in the semiconductor. The band filling effect occurs with the electron transition from the ground states to excited states induced by laser irradiation having an energy near the band gap, Eg. Excitation by electrons widen the band gap from Eg to Eg' (Eg'>Eg).

Therefore the absorption edge shifts to high energy, and then a blue shift of the absorption spectrum occurs. Consequently the absorption coefficient decreases. The refractive index also decreases in the lower energy region and it increases in the higher energy one.

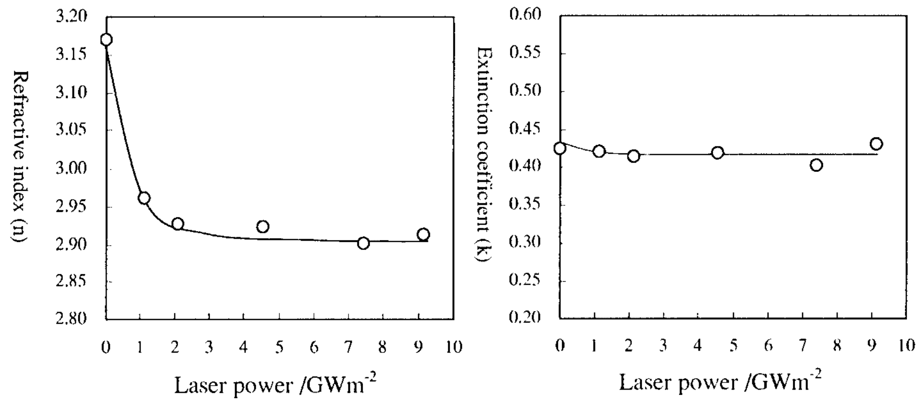

Figure 2 Laser power dependence of refractive index and extinction coefficient of $84Co_3O_4$-$8SiO_2$-$8TiO_2$ thin film.

Since we use the laser that has a 650nm wavelength (E=1.91eV) in the present study, it is considered that the laser excited the electrons corresponding to the band gap of 2.06eV. Laser energy of 1.91eV is lower than the Eg of 2.06eV, so the refractive index also decreases.

Response time of the change of refractive index by the band filling effect was reported to be on the order of nano second in semiconductors [13]. Measured response time in the present study is also on the order of a nano second, so we have good agreement with the reported value.

Next, we consider the relation between the band structure and the reaction with the laser. Co_3O_4 has a spinel structure in which Co^{2+} ions occupy the four-coordinate tetrahedral sites and Co^{3+} ions are in the six-coordinate octahedral sites. Such a complex structure gives many localized bands, and there are several absorption peaks. The absorption band corresponding to Eg=2.06 eV is assigned as a charge transfer from $O^{2-}(\pi^*\Gamma)$ to $Co^{2+}(\sigma^* t^2)$. The laser having E=1.91eV excites this transition. Therefore we consider that Co^{2+} in the Co_3O_4 spinel structure makes a large contribution to the optical nonlinearity.

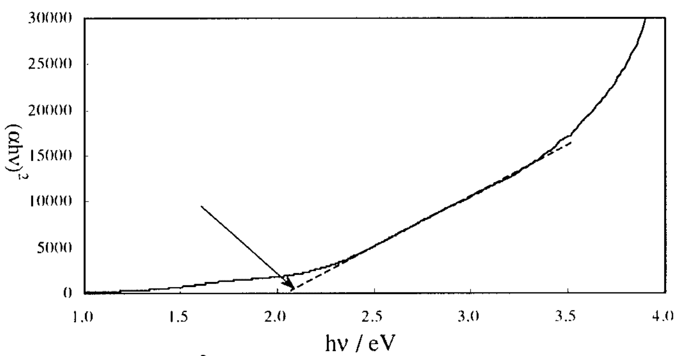

Figure 3 hν- $(\alpha h\nu)^2$ plots of $84Co_3O_4$-$8SiO_2$-$8TiO_2$ thin film.

CONCLUSIONS

Refractive index and extinction coefficient of Co_3O_4 with SiO_2-TiO_2 thin films in the ground state were 3.17 and 0.42, respectively. Both n and k decreased by irradiation of a pulse laser with 650 nm wavelength (1.91eV), and these values in the excited state were 2.91 and 0.41, respectively. n_2 was estimated from the change of n to be -2.8×10^{-11} m^2/W. The film had a band gap corresponding to 2.06eV, indicating that it was widened by the band filling effect during the laser irradiation at an energy of 1.91eV, and then the absorption coefficient and refractive index decreased.

ACKNOWLEDGMENT

This work was carried out in the Nanotechnology Glass Project as part of the Nanotechnology Materials Program supported by the New Energy and Industrial Technology Development Organization (NEDO).

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